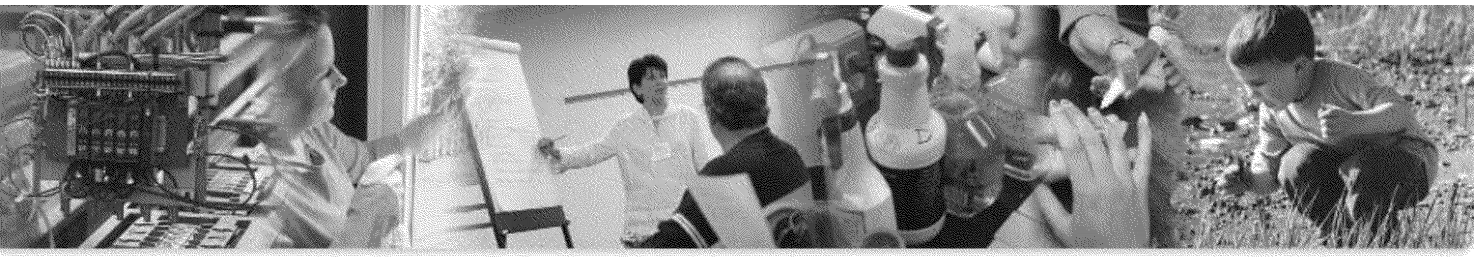

Safer and Effective Alternatives to Methylene Chloride For Paint Stripping Products

November 30, 2016

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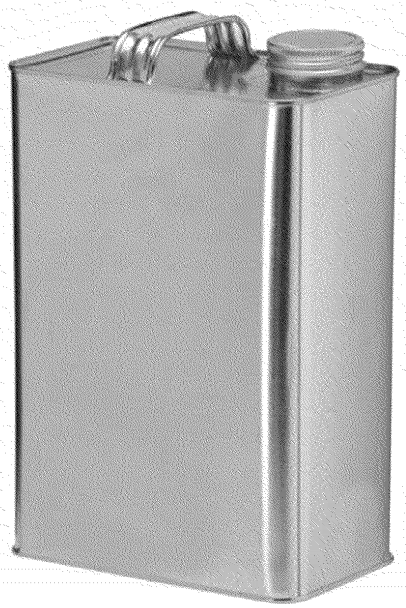
Paint Stripper Products



Approx. 2% - 5%
Additives: thickeners, wetting agents, colorants, rinsing agents, evaporation barriers, etc.

Approx. 95% - 98%
Solvent blends – to dissolve the various types of polymers used for paints/coatings

Methylene chloride, toluene, methanol blends
or
Solvent blends with benzyl alcohol, formic acid, *N*-Methyl-2-pyrrolidone (NMP), dibasic esters (dimethyl adipate, dimethyl glutarate, dimethyl succinate), MEK, triethyl phosphate, acetone, etc.

Methylene Chloride Based Paint Removers

PRODUCT NAME	MANUFACTURER	Methylene Chloride	Methanol	Toluene
Crown Tuff-Strip	*Packaging Service Co.*	65-67%	10-20%	0-5%
Dad's Easy Spray Paint & Varnish Remover	*Sansher Corp*	70-80%	5-10%	
Formby's Paint & Poly Remover	*Formby's*	81%	3%	
Green's Liquid - 96 Paint Remover	*Green Products, Co*	69-79%		
Green's Liquid Paint, Varnish & Lacquer Remover	*Green Products, Co*	10-30%		
Green's Semi-Paste Paint Remover	*Green Products, Co*	69-79%		
Jasco/Bix Varnish & Stain Remover	*W.M. Barr*	25-40%	30-50%	10-20%
Jasco Premium Remover	*W.M. Barr*	60-100%	10-30%	
Jasco Semi-Paste Varnish & Stain Remover	*W.M. Barr*	25-40%	30-50%	10-20%
Jasco Spray On Stripper	*W.M. Barr*	30-60%	15-40%	10-30%
Klean Strip Adhesive Remover	*W.M. Barr*	60-100%	10-30%	
Klean-Strip Premium Sprayable Stripper	*W.M. Barr*	60-100%	10-30%	
Klean-Strip Strip X Stripper	*W.M. Barr*	30-50%	10-30%	1-10%
Kutzit	*Savogran Company*	20-25%	20-25%	25-30%
Piranha 2	*Fiberlock Technologies*	Unknown	Unknown	Unknown
Premium Stripper	*W.M. Barr*	70-90%	1-5%	
Strypeeze Original	*Savogran Company*	25-30%	25-30%	15-20%
Superstrip	*Savogran Company*	85-90%	5-10%	0-5%
5F5	*Savogran Company*	65-70%	10-15%	10-15%
Zar Paint & Varnish Remover	*United Gilsonite Labs*	90%	7%	2%
ZipStrip Contractors Plus Paint & Varnish Remover	*Absolute Coatings*	16%	31%	18%
ZipStrip Premium Paint & Finish Remover	*Absolute Coatings*	75-85%	7-15%	
ZipStrip Trigger Spray Paint & Varnish Remover	*Absolute Coatings*	<80%	10%	8%
ZipStrip Water-Rinsable Industrial Strength Paint & Finish Remover "		80%	10-15%	

California Department of Public Health, Hazard Evaluation System and Information Service - California Department of Industrial Relations - Rev. May 2014

http://www.cdph.ca.gov/programs/ohb/Pages/methylenechloride.aspx

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Methylene Chloride Based Paint Removers

Company	Product Name	Methylene Chloride	Methanol	Toluene
PPC	Paint Stripper	>60%	<10%	
W.M. Barr	Goof Off Pro Paint Stripper	60% - 100%	10% - 20%	
Reochem	Paint Stripper	>60%	10% - 30%	
Palace Chemicals	Strip Away Pro	70% - 90%	8%	
ITW Permatex	161DA Paint Stripper	40% - 70%	3% - 7%	
Zinnser	StripFast Power Stripper	% not disclosed	% not disclosed	

Caustic Paint Removers

PRODUCT NAME	MANUFACTURER	Sodium Hydroxide	Magnesium Hydroxide	Calcium Hydroxide
Piranha 8	*Fiberlock Technologies*	5-10%		20-30%
Peel Away 1	*Dumond Chemicals*	9%	16%	21%

Caustic strippers are water-based solutions with a pH of 13 – 14.

The health risks include severe skin and eye burns even on short contact. Inhalation can cause lung irritation.

Caustic strippers can darken wood and raise the grain.

California Department of Public Health, Hazard Evaluation System and Information Service - California Department of Industrial Relations - Rev. May 2014
http://www.cdph.ca.gov/programs/ohb/Pages/methylenechloride.aspx

NMP Based Paint Removers

Company	Product	Benzyl Alcohol	Dibasic Esters (DMA, DMG, DMS)	Formic Acid	NMP	Other
Sunnyside Corp.	Ready Strip Pro Plus Paint & Varnish Remover	20% - 35%		2% - 15%	5% - 15%	
Sunnyside Corp.	Ultra Strip Ultimate Paint Removal		28% - 60%	1% - 2%	35% - 50%	
W.M. Barr	CitriStrip Stripping Gel		20% - 60%		30% - 60%	Citrus 1% -5%
Dumond Chemicals	Peel Away 5 Soy Based	20% - 50%			25% - 35%	Fatty acid methyl ester 15% - 20%
Dumond Chemicals	Peel Away 7	20% - 40%			10% - 20%	
Fiberlock Tech - nologies	Piranha 4		40% - 45%		45% - 50%	D-Limonene 0% - 5%

Paint Removers – Other

Company	Product	Benzyl Alcohol	Dibasic Esters (DMA, DMG, DMS)	Formic Acid	NMP	Other
Sunnyside Corp.	High Speed Ready Strip Citrus Paint & Varnish Remover	25% - 35%	9% - 21%	1% - 3%		Propylene gylcol 1% - 2%
Barrettine	Paint Panther Paint & Varnish Remover					MEK 5% - 10%, 1-methoxy-2-propanol 10% - 30%, 2-2 butoxy-ethoxy ethanol 5% - 10%
EZ Strip	EZ Strip Paint & Varnish Remover		18% - 47%			Triethyl phosphate 3% - 7%
Eco Solutions	Home Strip Paint and Varnish Remover					Triethyl phosphate 9.9%, water based
Besway Systems	Big "E" Industrial Paint Remover		35% - 50%			Aromatic solvent 10% - 15%, ethyl-3-ethoxy propionate 5% - 10%
Eco Safety Products	EcoFast Heavy Duty Paint Stripper	% Trade Secret				
Reochem	Paint Stripper Plus					Ethylene glycol <50%
Kansai Plascon	RemovALL All Purpose Paint Remover	<40%				

Paint Removers – Other

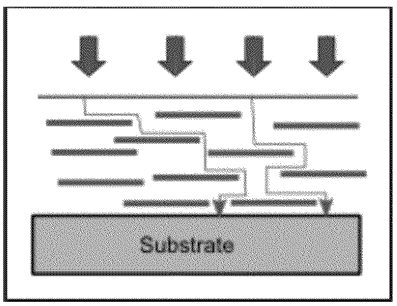
Company	Product	Benzyl Alcohol	Dibasic Esters (DMA, DMG, DMS)	Formic Acid	NMP	Other
Packaging Service Co.	Crown Paint Strip Next		60% - 90%			DMSO 20% - 25%
Sunnyside Corp.	Hi-Speed Ready Strip	25% - 35%	9% - 21%	1% - 3%		D-limonene 1% - 2%
Motsen-bockers	Lift off Paint and Varnish Remover					Acetone <10%, Glycol ether DB 10% - 20%
Solvent Kleene Peabody, MA	D-Zolve 15-33 IM	2% - 20%				Water based formulation
Fiberlock Technologies Andover, MA	Piranha Nextstrip Pro	30% - 40%		1% - 5%		
3M	Safest Stripper Paint and Varnish Remover		21% – 35%			
Dumond Chemicals	Smart Strip	30% - 50%				Water 40% - 60%

Paint Penetration

Paint penetration is important for removing multiple layers of paint in a single application of the paint stripper. The penetration of the multiple layers of paint and breaking the bond between the paint and substrate make it easy to remove all layers with a scraper.

Paint penetration is a function of molecular volume and Hansen hydrogen bonding parameter.

- The smaller the molecular volume, the better the paint penetration.
- The lower the Hansen hydrogen bonding parameter, the better the paint penetration.



Methylene Chloride Issues

Methylene chloride is a well-known and widely used component in paint strippers.

Due to its high volatility, the major route of exposure to methylene chloride is through inhalation. Exposure may also occur through ingestion or dermal absorption.

Methylene chloride is recognized as a carcinogen and has been linked to cancers of the brain, liver, and biliary tract. In the body, methylene chloride is also transformed into carbon monoxide, a known poison to the brain and nervous system.

There have been numerous worker deaths related to the use of methylene chloride stripping agents. Consumer deaths related to the use of methylene chloride paint strippers have also been documented.

The European Parliament banned the marketing of methylene chloride based paint strippers in the European Union effective June 2012, citing numerous deaths from acute methylene chloride poisoning specifically related to its use in paint strippers.

Source: California Environmental Protection Agency Department of Toxic Substances Control, Paint Strippers Containing Methylene Chloride, March 2014.

Issues with Non-MC Products

1. Toxicity: benzyl alcohol, 2-(2-butoxyethoxy) ethanol, dibasic esters (DMG, DMS, DMA), d-Limonene, acetone, MEK, and formic acid are all Green Screen Benchmark 2 chemicals, NMP is toxic to reproduction

2. Solvency difficulties: Hansen Solubility Parameters are far from optimized values.

3. Coating penetration difficulties: Due to large molecular volume, limited water solubility for water blends, and/or high hydrogen bonding values.

Chemical	Mol. Volume
Benzyl alcohol	104
Dimethyl glutarate	152
Dimethyl adipate	168
Dimethyl succinate	135
d-Limonene	163
Triethyl phosphate	171

- Strips paint one layer at a time
- Multiple applications required
- Longer dwell times required

Requirements for Alternative

1. **Toxicity:** Be comprised of chemicals that are safer from an environmental, health, and safety standpoint as compared to methylene chloride
2. **Solvency:** Have desirable Hansen Solubility Parameters to be an effective solvent for a wide range of coatings -paint (oil, latex), varnish, lacquer, shellac, epoxy, and polyurethanes
3. **Paint Penetration:** Be comprised of chemicals that have small molecular volumes (similar or close to the methylene chloride molecular volume of 64.4), and also have low hydrogen bonding values
4. **Substrates:** Efficacy on the following substrates: wood, metal, and masonry, also will not stain wood or raise the wood grain
5. **Cost:** Raw material cost less than approx. $0.70 per pound
6. **Viscosity:** Ability to cling to vertical surfaces (after addition of thickener)
7. **VOC content:** Less than 50%

Hansen Solubility Parameters: Inter-molecular forces

Dispersion force (also called London Force)

- The electron cloud surrounding an atom is, on average, evenly distributed around the atom.
- However at a given moment, the electron distribution may not be even.
- This causes a temporary, non-localized (disperse) polarization force. This is a component of the van der Waals force.

Polar force (also called dipole-dipole force)

- Dipole moments are created when atoms of the same molecule have different electronegativities.
- This causes a permanent polarization, from a specific, fixed location.

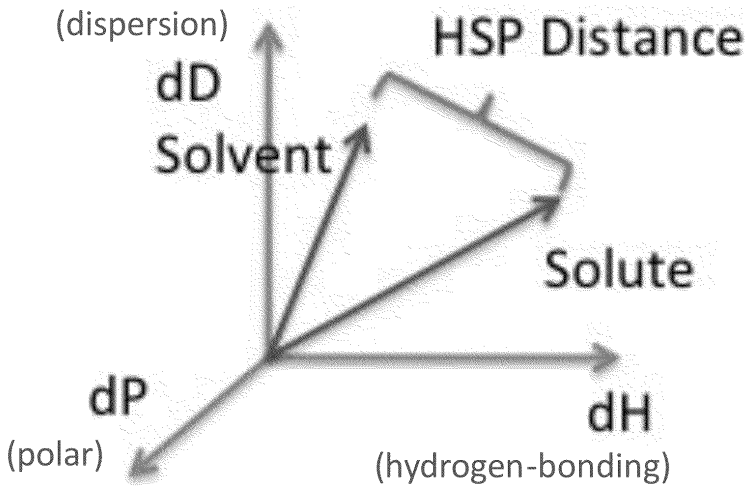
Hydrogen bonding force

- Occurs in molecules containing highly electronegative elements (i.e. F, O, or N) directly bound to hydrogen.
- This force exists between hydrogen atoms and other atoms present in adjacent molecules.

Strength of forces (on average): hydrogen bonding > polar > dispersion

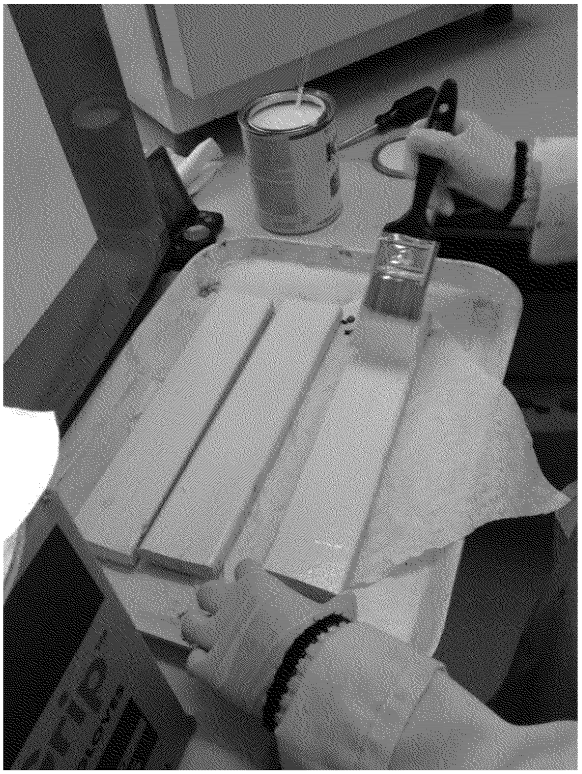
“Like dissolves like”

Determined the optimal target D, P, H values derived from a model containing HSP values for 59 different types of coatings/manufacturers (including alkyd, amino resin, cellulose acetate, epoxy, polyacrylate, polyamide, polyester, polyurethane, polyvinylbutyral, chlorinated polypropylene, polyvinylacetate, shellac, silicone, and methacrylate)



Source for figure: https://pirika.com/NewHP/PirikaE/polymer-solvent.html

Test Coupon Preparation



Substrate:
white pine

Coupon Sizes:
2.5” wide x 12” long
3.5” wide x 15” long

Coatings:
1 primer coat
4 – 6 finish coats
Lightly sand with 100 grit sandpaper and wipe clean with isopropyl alcohol before each coating

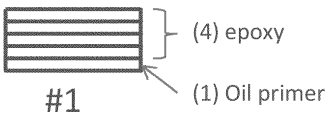
Aging:
3 weeks in oven at 140 F (to simulate 11 months of aging)

Test Coupon Preparation

	ASTM Standard D6189	UMass Lowell Approach	Comments
Primer layer	None	Yes (1 layer)	
# coating layers	3	4 (6 for mixed coupon)	
Total layers: primer + coating layers	3	5 (7 for mixed coupon)	Better indication of multi layer stripper performance
Preparation between layers	None	Light sand, alcohol wipe clean	To promote better adhesion between coating layers
Thermal aging	None	3 weeks in oven at 140 F	Simulate 11 months of aging

ASTM Standard D6189: "Standard Practice for Evaluating the Efficiency of Chemical Removers for Organic Coatings"

Oil Primer Test Coupons



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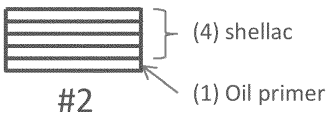

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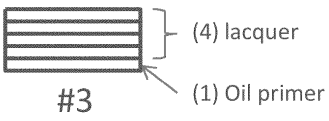

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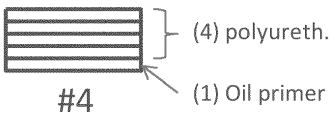

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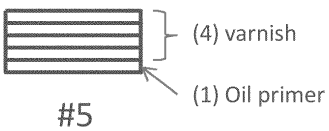

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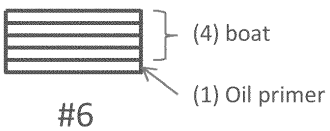

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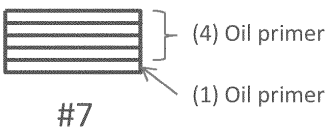

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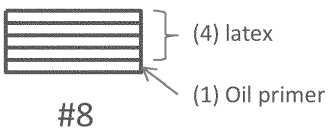

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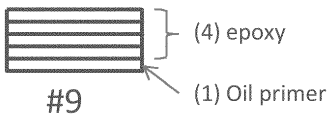

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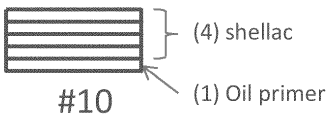

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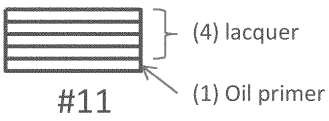

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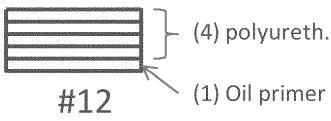

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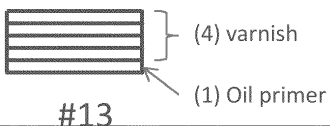

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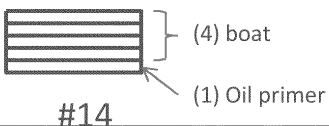

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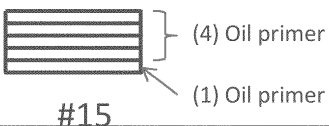

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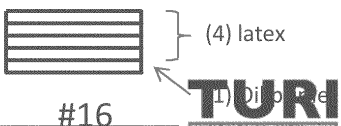

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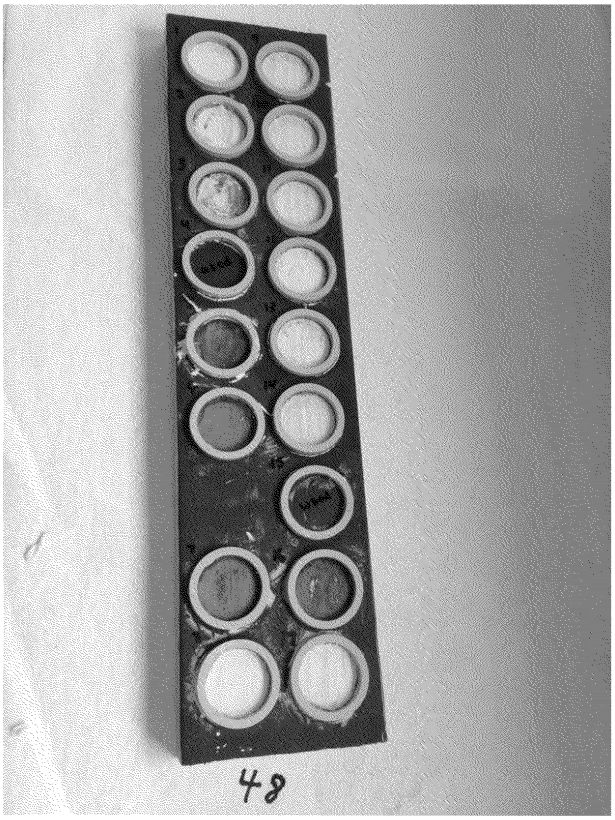
Test Coupon 48

Polyurethane
Polyurethane
Oil topcoat (grey)
Latex topcoat (red)
Oil topcoat (grey)
Latex topcoat (red)
Oil primer (white)
Wood substrate

#48



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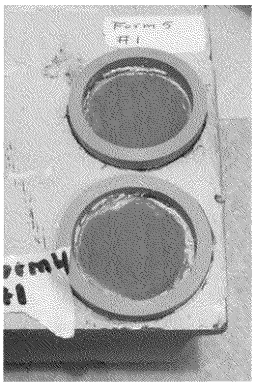
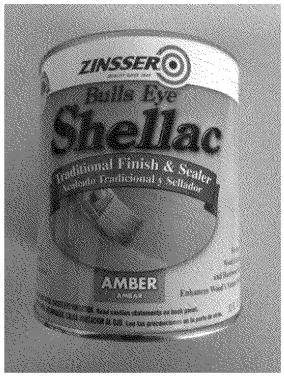
Testing Procedure

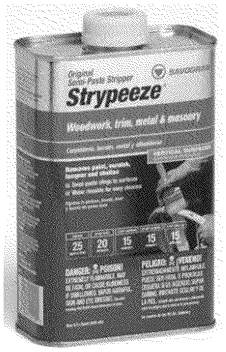


- Glue a ring gasket on the test area of the test vehicle
- Use a clean pipette to add approx. 1.5 ml of solvent blend inside the ring gasket
- Cover the gasket with lab watch glass
- Start timer to initiate dwell time
- Record initial cracking time
- After dwell time: remove watch glass
- Lightly scrape off coating residue with plastic scraper & record substrate exposure

Coatings

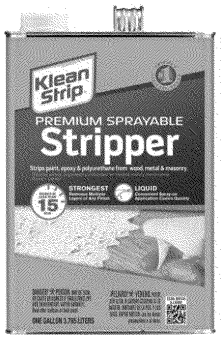


Methylene Chloride Based Paint Strippers Tested



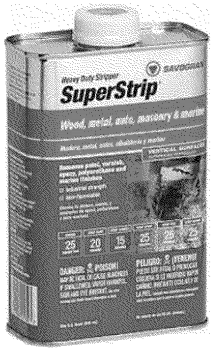
Strypeeze:

- Methylene chloride (25% – 30%), methanol (25 – 30%), toluene (15 – 20%), and acetone (15 – 20%).



Klean Strip Stripper:

- Methylene chloride (60% – 100%), methanol (15 – 25%).



SuperStrip:

- Methylene chloride (85% - 90%), methanol (5 – 10 %), and toluene (0 – 5%).

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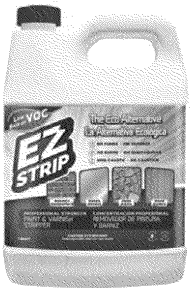
Alternatives Tested

NMP, Benzyl Alcohol, & Formic Acid

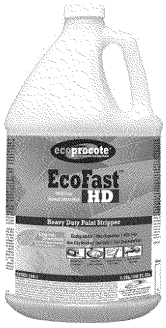


DMG, DMA, DMS, Triethyl phosphate

Acetone/glycol ether

NMP, DMG, DMA, DMS

NMP, Benzyl Alcohol



Benzyl alcohol

Benzyl alcohol, water

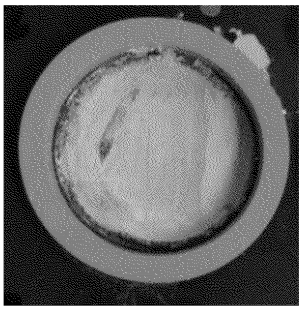
University of Massachusetts Lowell Formulations

Formulation	Solvents	Approx. Cost ($ per lb)
Formulation 4	Methyl acetate DMSO Thiophene	$0.94
Formulation F	Methyl acetate DMSO	$0.59

Patent application filed August, 2016.

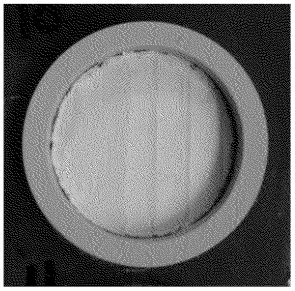
Test Results – Example

0% (bold) substrate exposure
(top layer not affected)



60% substrate exposure

0% substrate exposure
(some layer(s) removed)



95% substrate exposure

Test Results Summary: % Substrate Exposure

Coup-on	Dwell Time (min)	Stryp-eeze	Super Strip	Klean Strip	UML Form 4	UML Form F	Eco-Fast	Peel Away	Citri-Strip	Ready Strip	EZ Strip	Lift-Off	Smart Strip
Epoxy (4)	20, 10	80	95	99	80	75	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Shellac (4)	8	65	75	70	70	20	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Lacquer (4)	10	77.5	95	85	95	65	0	0	0	0	0	0	0
Polyur. (4)	10	95	85	85	95	72	**0**	**0**	**0**	0	**0**	**0**	0
Varnish (4)	20, 12	85	85	85	80	80	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Oil (4)	25, 10	95	90	95	70	75	**0**	**0**	**0**	**0**	**0**	**0**	**0**
Latex (4)	25	85	80	85	70	60	0	0	0	0	0	0	0
O,L,P (2,2,2)	20, 15	82.5	90	85	60	70	0	0	0	0	0	0	0
Aver-age		83	87	86	78	65	0	0	0	0	0	0	0

All coupons have one layer of oil based primer.

Current Status

- One year EPA People, Prosperity, and the Planet Phase I Award (August 2016 to August 2017) with four UMass Lowell students
- Evaluate thickeners to include in the formulation
- Conduct performance testing on different substrates (metal, masonry, non-pine wood)
- Perform toxicity screening tests on solvent blend
- Identify industry partner to commercialize new paint stripper product
- Confidentiality agreement required to share % ranges of UMass Lowell formulations, thickener test results, detailed test results, and bring formulations to industry partner for evaluation